Influence of Potassium Doping on the Formation of Vanadia Species in V/Ti Oxide Catalysts

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The influence of potassium on the formation of surface vanadia species on V/Ti oxide catalysts containing from 0.2 to 5 monolayers of vanadia (K/V atomic surface ratio ≤1) has been investigated by temperature programmed reduction in hydrogen and by FT-Raman spectroscopy under dehydrated conditions. In the pure catalysts, monomeric and polymeric (metavanadate-like) species, "amorphous" and bulk crystalline V_2O_5 were detected depending on the surface vanadia loading. In the K-doped catalysts, vanadia species formed on the surface depend also on the K/V atomic ratio. Even at small K/V ratios, K inhibits the formation of the polymeric species in favor of the "K-doped" and/or "K-perturbed" monomeric species. These species possess lengthened V═O bonds with respect to the monomeric species in the undoped V/Ti oxides. At K/V = 1, the "K-doped" monomeric species and "amorphous" KVO_3 are mainly present on the surface. Reduction of vanadia forms in the K-doped catalysts takes place at higher temperatures than in the catalysts where potassium was absent. The monomeric and polymeric species, which are the active sites in partial catalytic oxidation, have the lowest reduction temperature. Vanadia species formed on the commercial titania, containing K, were also elucidated. The catalysts were characterized via X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and Brunauer−Emmett−Teller surface area measurements.

Introduction

V/Ti oxides are widely used catalysts in selective oxidation of hydrocarbons and reduction of NO_x. Recent European Catalysis Community reports[1,2] have focused on the design and characterization of V/Ti oxide catalysts. Laboratory prepared high-purity V/Ti oxide was studied in detail.[3−5] The results of these studies indicate that a two-dimensional vanadia layer is the active phase in selective oxidation of hydrocarbons since it shows a higher activity and selectivity than bulk V_2O_5 crystallites. This layer consists of isolated monomeric and polymeric (metavanadate-like) species with tetrahedrally coordinated vanadium. With increase in vanadia coverage, formation of bulk crystalline V_2O_5 particles and "amorphous" multilayered vanadia was observed.[4] The factors determining the structure of vanadia species on titania are (i) the concentration of vanadia, (ii) the catalyst pretreatment, and (iii) the presence of additives on the titania surface. The titania structure and its surface area did not affect the type of surface vanadia species observed.[6]

Little information is available on the structure of the vanadia species for doped catalysts and catalysts prepared on commercial TiO_2 supports. One of the main impurities in commercial titania is potassium.[3,4,7] By Raman spectroscopic studies Wachs et al.[3,8] found that K increases the length of V═O bond in the isolated monomeric vanadia. The same conclusion follows from the FT-IR spectroscopy data.[9,10] Grzybowska et al.[4,11,12] introduced K before and after vanadia deposition on titania and showed that the properties of the resulting V/Ti oxide catalysts depend on the order of deposition. In our previous study[13] it was found that K addition introduces disorder in the bulk crystalline structure leading to a better spreading of V_2O_5 on TiO_2 surface. Formation of KVO_3 was detected, being in agreement with reported results.[11,12,14] Other vanadates have also been found in K-doped V/Ti oxides.[12,14] It has been shown that supported alkali vanadates could be used as catalysts for partial oxidation of ethane.[15]

Vanadia in the pure V/Ti oxides exists in different forms, which are present in small concentrations on the catalyst surface. By only a spectroscopic method it is difficult to establish a relationship between the structure of surface sites and their reactivity. The temperature-programmed reduction in hydrogen (TPR)[16−18] combined with spectroscopic characterization of surface vanadia allows relating the reactivity of surface species. TPR is a suitable technique for the determination of surface reducibility. The majority of catalytic oxidation reactions are known to proceed via the Mars−van Krevelen (redox) mechanism. A correlation is often observed between the reducibility of vanadia species and activity in partial oxidation of hydrocarbons. For example, vanadia supported on titania

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Table 1. Characteristics of the Studied Catalysts

sample	V, wt %	K/V atomic ratio	S_{BET}, m^2/g	vanadia monolayers[a]
Model Catalysts on the Laboratory TiO_2				
0.2 monolayer V/TiO_2 (K/V = 0)	1.2	0	76	0.19
0.2 monolayer V/TiO_2 (K/V = 0.25)	1.2	0.25	77	0.22
0.2 monolayer V/TiO_2 (K/V = 1)	1.4	1	69	0.24
2 monolayer V/TiO_2 (K/V = 0)	8.1	0	56	1.7
2 monolayer V/TiO_2 (K/V = 0.05)	7.2	0.05	50	1.5
2 monolayer V/TiO_2 (K/V = 0.25)	6.9	0.25	39	2.1
5 monolayer V/TiO_2 (K/V = 1)	7.3	1	16	5.3
Catalysts on the Commercial (Aldrich) TiO_2				
0.35 monolayer V/TiO_2 (K/V = 1)	0.27	1[b]	9	0.35
0.62 monolayer V/TiO_2 (K/V = 0.57)	0.47	0.57[b]	9	0.62
0.75 monolayer V/TiO_2 (K/V = 0.47)	0.57	0.47[b]	9	0.75
3.7 monolayer V/TiO_2 (K/V = 0.1)	2.8	0.1[b]	9	3.7

[a] Monolayer is taken equal to 10 V atom/nm^2.[4] [b] Determined by XPS.

is easier to reduce than pure V_2O_5 and vanadia supported on some other supports (SiO_2, Al_2O_3, MgO, etc.).[19] The catalytic activity trend in the partial oxidation of methanol,[20] toluene,[21] and ethane,[22] and in the oxydehydrogenation of propane[23] correlates well with the catalyst reducibility. Similarly K and P are reported to decrease both the reducibility of V/Ti oxide in hydrogen and the catalytic activity in toluene and *o*-xylene oxidation.[7]

It is important to note that a lot of spectroscopic studies of V/Ti oxides have been performed under ambient conditions[11,12,14,24−26] without controlling humidity, despite the known dependence of vanadia species on the presence of water vapor. Under hydrated conditions (a) lengthening of the V═O bond, (b) transformation of different vanadia species on the surface, and (c) change of the vanadium atom coordination have been reported.[3,27−29]

The objectives of the present work are twofold: (i) first, to find a correlation between the reducibility of the titania supported vanadia, characterized by TPR in H_2 and the vanadia structure, characterized by FT-Raman spectroscopy under dehydrated conditions; (ii) second, based on the results obtained, to determine the structure of vanadia supported on commercial TiO_2 (Aldrich) containing K. The catalysts on the base of Aldrich titania support were found to be efficient in benzaldehyde formation from toluene under anaerobic conditions.[13,30] Some catalysts were additionally characterized by high-resolution transmission electron microscopy (HRTEM), ^{51}V magic angle spinning (MAS) NMR,[13] and X-ray photoelectron spectroscopy (XPS).

Experimental Section

Catalyst Preparation. Two series of V/Ti oxides were prepared (Table 1). The first one called "model catalysts" was prepared by vanadia deposition on a laboratory TiO_2 obtained by hydrolysis of the tetrapropyl orthotitanate (>98%, Fluka). In the second series, vanadia was supported on a commercial TiO_2 (Aldrich) containing K (0.2 wt %), as determined by atomic absorption spectroscopy (AAS) (Perkin-Elmer 1100). X-ray diffraction (XRD), Raman spectroscopy, and HRTEM studies showed that both supports possess an anatase crystalline structure.

The laboratory TiO_2 was washed in diluted nitric acid (1.2 N) to remove surface impurities before vanadia deposition. Catalysts were prepared via wet impregnation using vanadium oxalate solution (synthesized from V_2O_5 (>99.6%, Aldrich) and oxalic acid (>97%, Fluka)). The support was kept in the minimal amount of solution for 3 min, then the excess of solution was filtered. The catalysts with high concentration of vanadia (7−8 wt %) were prepared via multistep wet impregnation with short calcination between the steps (30 min, 723 K in air). K-doped V/Ti oxides were prepared via coimpregnation of vanadium oxalate and potassium oxalate (purum, Fluka). After drying, the samples were calcined for 120 min at 723 K in air.

The concentration of vanadium in the catalysts listed in Table 1 is expressed by monolayers of the titania coverage by VO_x species (1 monolayer = 10 V atoms/nm^2).[4] Surface impurities were not found by XPS in the undoped catalysts.

Catalysts based on the commercial TiO_2 (Aldrich) with 0.27, 0.47, and 0.57 wt % V content were prepared via well-known grafting techniques.[4,31] The 2-, 5-, and 10-step vapor-phase deposition of $VOCl_3$ (293 K) onto the TiO_2 surface was followed by hydroxylation (wet air, 340 K), drying, and calcination (2 h, 723 K). Impregnation of vanadium oxalate from aqueous solution was used to obtain a catalyst with 2.8 wt % of V. Potassium was the only impurity in the catalysts found by XPS.

Temperature-Programmed Reduction. A Micromeritics AutoChem 2910 analyzer with a quartz plug-flow reactor was used for the TPR studies. The products in the reactor outlet were analyzed by a ThermoStar quadrupole mass spectrometer (Pfeiffer Vacuum). The gas flows were maintained constant throughout the experiments at 20.2 mL (STP)/min. Before the TPR, the catalysts were pretreated in oxidative atmosphere (2 vol % O_2, rest He) at 673 K for 30 min and then cooled to 323 K. After the purge by Ar, the reactor was heated in a flow of 4 vol % of H_2 in Ar with a heating rate of 20 K/min. The thermocouple was inserted into the middle section of the catalytic bed. The catalyst charge corresponded to 10−60 μmol of vanadium and the conversion of hydrogen was below 25%.

Catalyst Characterization. Raman spectroscopy experiments were performed by a FT-Raman 2000 spectrometer (Perkin-Elmer) equipped with a thermal background filter and Nd:YAG laser, operating at 1064 nm with a varying power in the range of 10−750 mW. FT-Raman spectroscopy is known by a smaller contribution of the sample fluorescence to the spectra as compared to conventional Raman spectroscopy,[32,33] which some-

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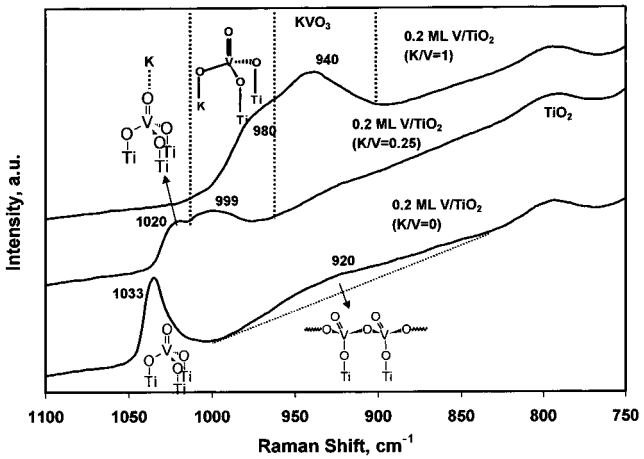

Figure 1. FT-Raman spectra of the 0.2 monolayer V/TiO_2 catalysts (laboratory TiO_2, anatase) with different K/V ratio.

times makes the measurements difficult. A Raman cell[34] was attached to the setup described elsewhere.[35] The measurements were performed in the Raman cell under the controlled atmosphere (dehydrated conditions[3]) in a flow of dry 20 vol % O_2/Ar mixture (60 mL (STP)/min) at 363−523 K. From 32 to 256 scans were averaged with a resolution of 4 cm^{-1} to obtain a spectrum. The catalysts were pretreated in this mixture at 673 K during 30 min. This pretreatment is similar to the one performed before the TPR experiments and gives an oxidized state of the catalyst.

XPS of the catalysts was obtained by a PHI 5500 ESCA system (Perkin-Elmer) with monochromated Al Kα radiation (1486.6 eV). The investigation of the surface morphology was carried out via an electron microscope (HRTEM, HF-2000, Hitachi). The maximum resolution of the instrument is 0.14 nm at the accelerating voltage 200 kV. A slow-scan Gatan CCD camera (1024 × 1024 pixels) allowed taking images at weak beam intensity minimizing the damage of the sample by the electron beam.

Results and Discussion

Model Catalysts with a Vanadia Concentration Less Than a Monolayer. As already mentioned in the Experimental Section, the model V/Ti oxides were prepared from the laboratory titania. Raman spectra of the 0.2 monolayer V catalysts are shown in Figure 1. The Raman spectrum of the catalyst without potassium is typical for the V/Ti oxides with low vanadium content.[8,27,36] It contains isolated monomeric species (1033 cm^{-1}) and polymeric (metavanadate-like) species (920 cm^{-1}). In all of these species, V^{5+} is tetrahedrally coordinated and attached to the titania surface via V−O−Ti bonds. The TPR trace of this sample (Figure 2) shows one peak at 767 K in agreement with the literature results.[17,18,24,31] The monomeric and polymeric species are reduced easily by hydrogen at the same temperature. The reduction activation energy of 98 kJ/mol was calculated from the maximum rate of reduction obtained at four different heating rates (5−64 K/min). A Raman spectroscopy study of the polymeric and monomeric species has reported that they disappear simultaneously in hydrogen.[36]

Doping of vanadia by K results in a considerable change in the Raman spectra and TPR profiles. Vanadia in the K-doped catalysts is reduced at higher temperatures as compared to the V/Ti oxide without K (Figure 2). The broadness of the TPR peak for the catalyst with K/V = 0.25 indicates the reduction of a multitude of surface

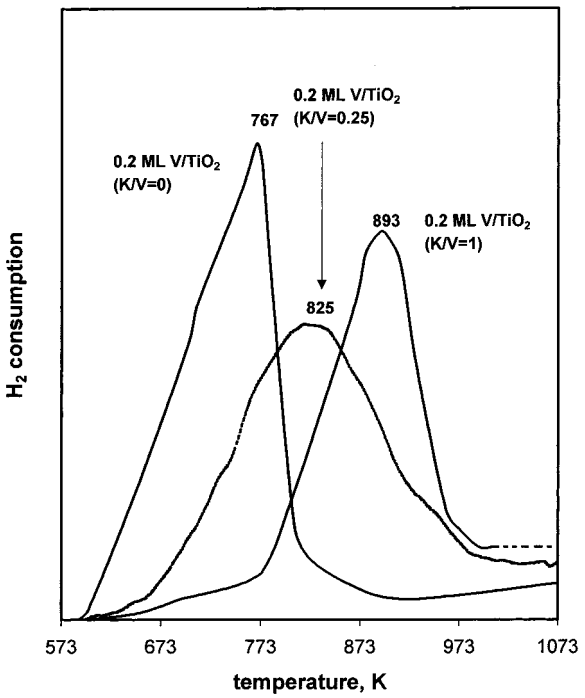

Figure 2. TPR profiles of the 0.2 monolayer V/TiO_2 catalysts (laboratory TiO_2, anatase) with different K/V ratio.

vanadia species. In the Raman spectrum of this catalyst (Figure 1) the band at 920 cm^{-1} (polymeric metavanadate like species) disappears, the band at 1033 cm^{-1} (monomeric species) shifts to 1020 cm^{-1}, and a new band concomitantly appears at 999 cm^{-1}.

The shift of the high-frequency band indicates a lengthening of the V=O bond due to the presence of potassium. An electrostatic interaction, $(Ti-O-)_3V=O^{\delta-}\cdots K^{\delta+}-O$, may be the cause of the observed perturbations. Hence, the band at 1020 cm^{-1} is assigned to the K-perturbed monomeric species. At K/V = 0.25 part of the bridging Ti−O−V=O sites could be substituted by K−O−V=O sites as proposed by Ramis et al.[9] The band at 999 cm^{-1} is assigned to this K-doped monomeric species. The disappearance of the 920 cm^{-1} indicates that K inhibits formation of polymeric metavanadate-like species with predominant formation of K-doped monomeric species.

Increase of the K/V ratio to 1 leads to further changes in the Raman spectrum. The 1020 cm^{-1} band disappears, the band at 999 cm^{-1} is shifted to 980 cm^{-1} due to an increased interaction with K, and a new band at 940 cm^{-1} appears. The latter band is similar to that of bulk crystalline KVO_3 (Figure 3a) but is much broader. It is assigned to "amorphous" KVO_3 implying small crystalline particles or a thin amorphous layer[13] observed by HRTEM for a K-doped catalyst. The TPR peak at 893 K seems to correspond to the reduction of this form (Figure 2). The reduction temperature of the "amorphous" KVO_3 differs from the one of the bulk crystalline KVO_3 (Figure 3b). According to the literature data,[25,37,38] the coordination of vanadium remains tetrahedral upon the addition of K. However, it is seen in Figure 2 that the reduction temperature increases noticeably upon K-doping as compared to the sample without K.

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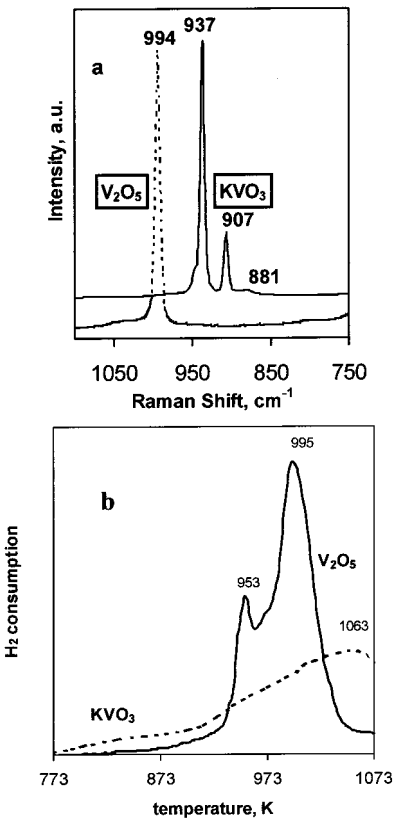

Figure 3. TPR profiles (b) and FT-Raman spectra (a) of V_2O_5 (>99.6%, Aldrich) and KVO_3 (laboratory synthesized).

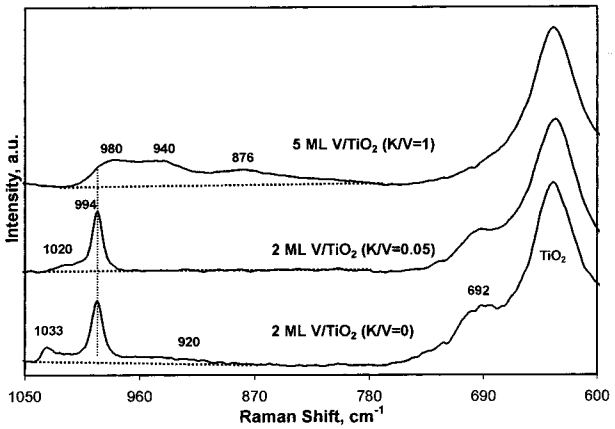

Figure 4. FT-Raman spectra of the V/TiO_2 catalysts (laboratory TiO_2, anatase) with high content of vanadia and different K/V ratio.

Model Catalysts with a Vanadia Concentration Higher Than a Monolayer. At a vanadium content of 2 monolayers, the bulk crystalline V_2O_5 is formed on the surface as seen from the Raman spectrum of the catalyst without K (bands at 994 and 692 cm^{-1}, Figure 4). The band of the monomeric species (1033 cm^{-1}) and a broad feature in the range of the polymeric metavanadate-like species (920 cm^{-1}) are also observed. The TPR profile of this catalyst shows a large peak at 840 K and a small one at 963 K (Figure 5). The 963 K peak corresponds to the reduction of the bulk crystalline V_2O_5 (953−995 K, Figure 3b). The peak at 840 K is assigned to the reduction of "amorphous" V_2O_5 in the form of thin layers[34,39] or small particles.[24] Reduction of the monolayer species found by

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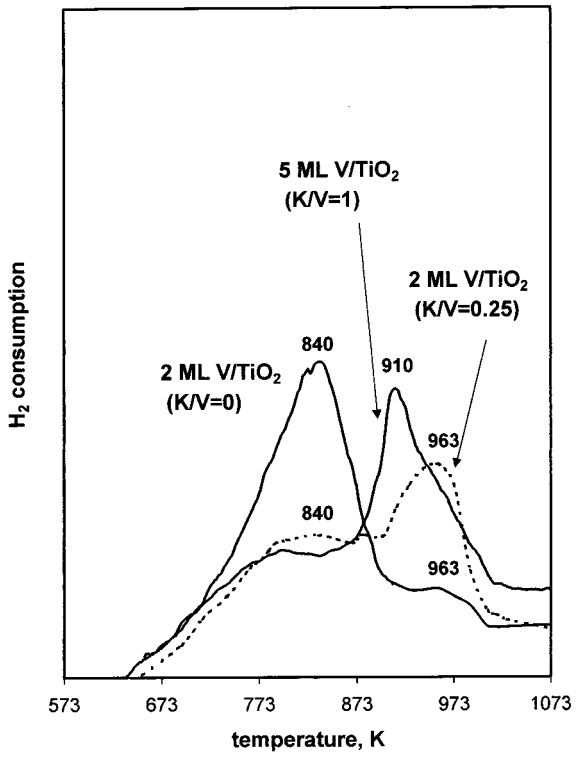

Figure 5. TPR profiles of the V/TiO_2 catalysts (laboratory TiO_2, anatase) with high content of vanadia and different K/V ratio.

Raman spectroscopy contributes to this peak at the lower temperature wing as compared to the TPR profile of the 0.2 monolayer V/TiO_2 catalyst (Figure 2).

Doping by K significantly changes TPR profiles (Figure 5) and Raman spectra (Figure 4). At K/V = 0.05, the 1033 cm^{-1} band shifts to 1020 cm^{-1} and the broad feature at 920 cm^{-1} disappears similarly to the 0.2 monolayer V/TiO_2 catalyst with K/V = 0.25 (Figure 1). The band characteristic for V_2O_5 is not perturbed by this small K addition. At K/V = 1 and a vanadia loading of 5 monolayer (Figure 4), the Raman spectrum resembles the one of the sample with low vanadia loading at ratio K/V = 1 (0.2 monolayer of V/TiO_2, Figure 1). The band at 980 cm^{-1} is assigned to the K-doped monomeric species and KVO_3 gives rise to the band at 940 and 876 cm^{-1} as they are observed in the spectrum of KVO_3 (Figure 3a). Bulk crystalline KVO_3 can be expected at this K/V ratio based on the literature XRD and phase diagram data.[14] The shoulder at 994 cm^{-1} is assigned to V_2O_5 probably existing in a small concentration.

The TPR profiles of the K-doped catalysts include several reduction processes with maxima at around 840, 910, and 963 K (Figure 5). None of these peaks could be assigned to the reduction of bulk crystalline KVO_3, because its maximal reduction temperature is higher (~1023 K, Figure 3b). The reduction process at 963 K is assigned to bulk crystalline V_2O_5 similarly to that for the undoped V/Ti oxide catalyst (Figure 5) and V_2O_5 (953−995 K, Figure 3b). The signal at 910 K corresponds to the reduction of "amorphous" KVO_3. The peak at around 840 K (Figure 5) probably is due to the reduction of the K-doped monomeric species together with the reduction of the "amorphous" V_2O_5. A similar reducibility of these two forms explains the same intensity of the peak at 840 K for the catalysts with the K/V ratio of 0.25 and 1.

Commercial Titania with a Vanadia Concentration Higher Than a Monolayer. As was mentioned above the Aldrich titania contains K as an impurity, which

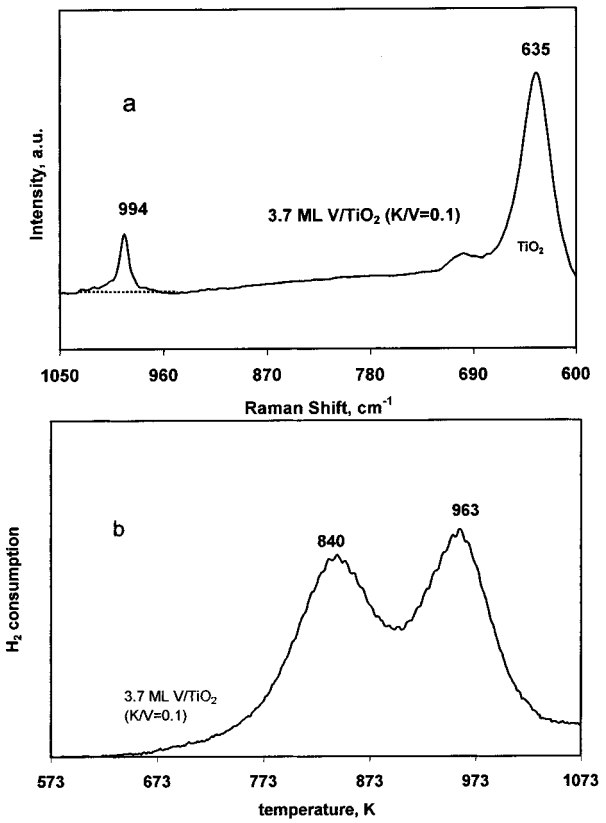

Figure 6. TPR profile (b) and FT-Raman spectrum (a) of the 3.7 monolayer V/TiO_2 catalyst ($K/V = 0.1$, Aldrich TiO_2, anatase).

should influence the properties of the V/Ti oxides. To elucidate the surface vanadia species formed on this support, the TPR and Raman spectra are compared with spectra of the model catalysts (undoped and K-doped). The Raman spectrum of the 3.7 monolayer of V/TiO_2 ($K/V = 0.1$) catalyst is depicted in Figure 6a. The 994 cm^{-1} band, characteristic for the bulk crystalline and "amorphous" V_2O_5 is seen. V_2O_5 was observed for this catalyst by means of ^{51}V MAS NMR as a most abundant species.[13] Bulk crystalline V_2O_5 particles were also found on the surface of this catalyst by HRTEM.[13]

Two reduction processes are observed in the TPR profile of the 3.7 monolayer V/TiO_2 catalyst (Figure 6b). The first reduction process (840 K, Figure 6b) is assigned to the reduction of the "amorphous" V_2O_5, similar to the undoped 2 monolayer V/Ti oxide (Figure 5) and the second reduction process is assigned to the reduction of bulk crystalline V_2O_5 (Figure 3). A higher contribution of the second process for this catalyst as compared with undoped 2 monolayer V/Ti-oxide (Figure 5) is explained by a higher vanadium surface concentration. A similar effect of the appearance

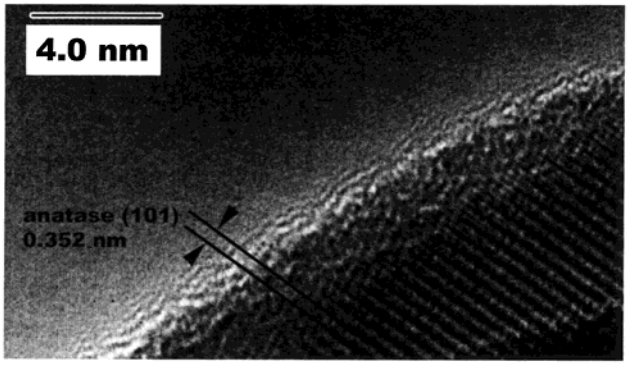

Figure 7. HRTEM image of the 0.75 monolayer V/TiO_2 catalyst (Aldrich TiO_2, anatase).

of the second reduction process upon the increase of the vanadium concentration is discussed by Bond and Tahir.[31]

Commercial Titania with a Vanadia Concentration Less Than a Monolayer. To understand the formation of surface species on the Aldrich titania at low vanadia loadings, three catalysts with 0.35, 0.62 and 0.75 monolayer of vanadia were prepared and characterized. XPS analysis gave the same K/Ti atomic ratio of 0.12 for the Aldrich titania and for the V/TiO_2 catalysts after vanadia deposition. In this series of catalysts, the K surface concentration is constant, but the K/V ratio changed with variation in V loading (Table 1).

HRTEM studies showed the absence of microcrystalline particles on the surface of titania for the 0.75 monolayer V/TiO_2 catalyst (Figure 7). The only crystalline structure found was bulk anatase-TiO_2 used as a support. These data point out that vanadia is in highly dispersed state.

TPR data (Figure 8) indicate at least two reduction processes at 853 and 910 K. Subtraction of the TPR trace of the 0.35 monolayer V/TiO_2 catalyst from those of the 0.62 and 0.75 monolayer V/TiO_2 catalysts results in an additional peak with a maximum at 800 K (Figure 8, inset). The intensity of the TPR signal at 800 K increases with increasing vanadia concentration (Figure 8, inset) and a corresponding decrease in the K/V ratio. Simultaneously, the band at 1020 cm^{-1} appears in the Raman spectra (Figure 9) assigned to the K-perturbed monomeric species.

The TPR peak at 853 K corresponds to the reduction of the K-doped monomeric species. The Raman band of this species is located at 990 cm^{-1} (Figure 9) laying between the bands at 980 and 999 cm^{-1} assigned to this species for the model K-doped V/Ti oxides supported on the laboratory titania (Figures 1 and 4). The TPR peak at 910 K is assigned to the reduction of the "amorphous" KVO_3 similar to that of the 0.2 monolayer V/TiO_2 catalyst with $K/V = 1$ (893 K, Figure 2). The corresponding Raman band at 960 cm^{-1} (Figure 9) is slightly higher than the one of the KVO_3 for the model catalyst (940 cm^{-1}) (Figure 1).

Table 2. Assignment of the TPR and Raman Peaks to Vanadia Species in the Undoped and K-Doped V/Ti Oxide Catalysts

TPR peak max, K	characteristic Raman band, cm^{-1}	assignment
	Undoped V/Ti Oxide Catalysts	
767	1033	monomeric species
767	920	polymeric (metavanadate-like) species
840	994	"amorphous" V_2O_5
963	994	crystalline bulk V_2O_5
	K-Doped V/Ti Oxide Catalysts ($K/V \leq 1$)	
800	1020	K-perturbed monomeric species
840	994	"amorphous" V_2O_5
853	990 ± 10	K-doped monomeric species
900 ± 10	950 ± 10	"amorphous" KVO_3
963 ± 10	994	crystalline bulk V_2O_5

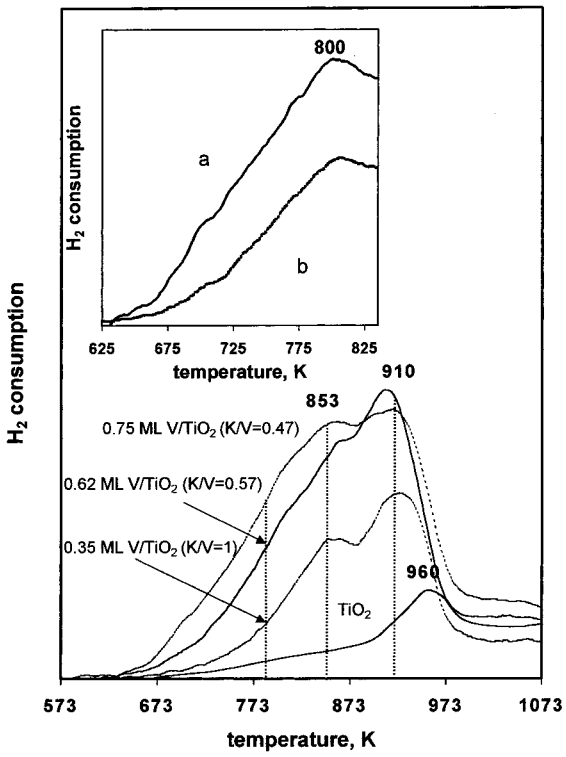

Figure 8. TPR profiles of the TiO_2 (Aldrich), 0.35, 0.62, and 0.75 monolayer V/TiO_2 catalysts (Aldrich TiO_2, anatase). K/V atomic surface ratio is indicated. On the inset figure the TPR profile of the 0.35 monolayer V/TiO_2 catalyst is subtracted from the ones of the 0.75 (a) and 0.62 (b) monolayer V/TiO_2 catalysts.

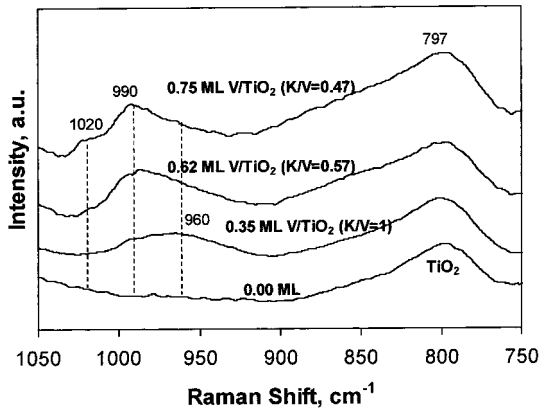

Figure 9. FT-Raman spectra of the TiO_2 (Aldrich) and V/TiO_2 catalysts (Aldrich TiO_2, anatase).

At temperatures higher than 960 K, the TPR profiles are explained by the reduction of the Aldrich titania support, since it has a similar TPR profile (Figure 8). The first peak during the reduction of titania is observed at around 960 K; however the reduction takes place mainly at temperatures higher than 1073 K.[19,24]

The results of this work are summarized in Table 2 and are also shown in the simplified scheme presented in Figure 10. V/Ti oxides without addition of potassium contain a mixture of the monomeric, polymeric species, "amorphous" and bulk V_2O_5 (Figure 10a). The ratio between these species depends on the total vanadia loading. The presence of alkali metals increases the basicity of the titania surface, which favors the tetrahedral coordination of vanadia species.[40] In the catalysts with K/V = 1, vanadia interacts with K forming K-doped

(40) Deo, G.; Wachs, I. E. *J. Phys. Chem.* **1991**, *95*, 5889.

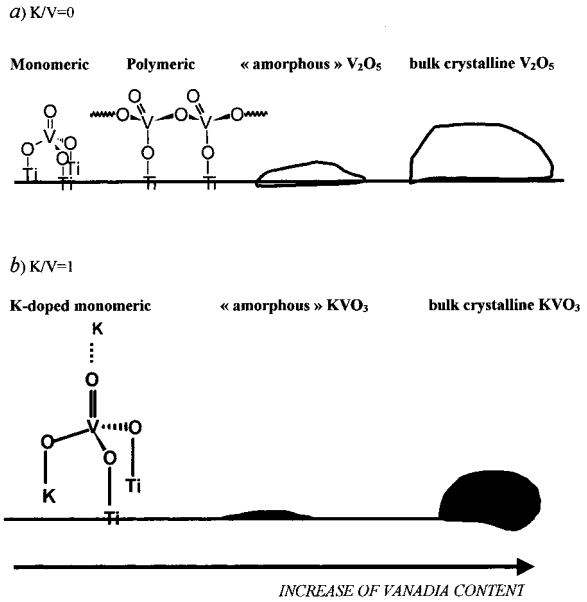

Figure 10. Schematic presentation of vanadia species formed in undoped V/Ti oxide (a) and K-doped (K/V = 1) V/Ti oxide (b) catalysts as a function of vanadia coverage.

monomeric vanadia and "amorphous" and bulk KVO_3 upon increased V-coverage (Figure 10b). As clearly seen in the Raman spectra of the 0.35 monolayer V/TiO_2 catalyst with K/V = 1 (Figure 9) and of the model 0.2 monolayer V/TiO_2 catalyst with K/V = 1 (Figure 1), undoped vanadia are not present. The same conclusion follows from the TPR profiles of these samples (Figures 2 and 8). Vanadia species typical for the pure catalysts appear only at ratios K/V < 1. The structure of monomeric species is perturbed by the presence of K resulting in the lengthening of their V=O bond (formation of the K-perturbed monomeric species) (1020 cm^{-1}, Figure 1). Therefore, the variety of vanadia species depends not only on vanadia concentration but also on the K concentration and the K/V ratio.

The formation of the K-doped monomeric species and "amorphous" KVO_3 in the K-doped catalysts could be responsible for the shift of the optimal activity toward higher vanadia coverage in respect to the pure catalysts.[3,4] Activity of the K-doped catalysts with K/V = 1 was found to be significantly lower in the toluene oxidation as compared to the undoped catalysts.[14] This observation should be taken into account during catalyst optimization.

Conclusions

Identification of the vanadia species in undoped and K-doped V/Ti oxides (K/V≤ 1) containing 0.2−5 monolayers of vanadia has been performed by TPR in H_2, FT-Raman spectroscopy under dehydrated conditions, HRTEM, and XPS. With increasing vanadia loading, monomeric and polymeric metavanadate-like species, "amorphous" and bulk V_2O_5 are formed on the surface of undoped V/Ti oxide. For the K-doped catalysts, the K/V ratio is another important factor determining the structure of vanadia species. Formation of polymeric metavanadate-like species, typical for the undoped catalysts, is inhibited by small addition of K. Monomeric species exist in the K-doped and/or K-perturbed forms with the lengthened V=O bond than the one in the monomeric species in the undoped V/Ti oxides.

At K/V = 1 mainly K-doped monomeric species and "amorphous" KVO_3 are present on the catalyst surface. At atomic ratios 0 < K/V < 1, a big variety of pure and K-doped vanadia species is observed.

Reduction of the K-doped monomeric vanadia species and "amorphous" KVO_3 takes place at higher temperatures than the reduction of vanadia species in the undoped catalysts. Monomeric and polymeric vanadia species are reduced more easily in the V/Ti oxide catalysts confirming that they can participate as active sites in partial oxidation reactions. The activation energy of 98 kJ/mol was obtained for their reduction in hydrogen.

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